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ORIGINAL PAPER

Fast and sensitive determination of captopril by voltammetric method using ferrocenedicarboxylic acid modified carbon paste electrode

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Abstract A ferrocenedicarboxylic acid modified carbon paste electrode was constructed and used as a fast and sensitive tool for the determination of captopril at trace level. It has been shown by direct current cyclic voltammetry and double step chronoamperometry that ferrocenedicarboxylic acid can catalyze the oxidation of captopril in aqueous buffer solution and produces a sharp oxidation peak current at about +0.49 vs. Ag/AgCl reference electrode. The square wave voltammetric peak currents of the electrode increased linearly with the corresponding captopril concentration in the range of 3.0×10^{-7}–1.4×10^{-4}M with a detection limit of 9.1×10^{-8} M. The influence of pH and potential interfering substances on the determination of captopril were studied. Electrochemical impedance spectroscopy was used to study the charge transfer properties at the electrode–solution interface. Finally, the sensor was examined as a selective, simple, and precise new electrochemical sensor for the determination of captopril in real samples, such as drug and urine, with satisfactory results.

Keywords Ferrocenedicarboxylic acid · Captopril · Electrocatalysis · Carbon paste electrode

Introduction

Captopril, 1-(3-mercapto-2-D-methyl-1-oxopropyl) proline (Scheme 1), an orally active inhibitor of the angiotensin-converting enzyme (ACE), has been widely used for the treatment of hypertensive diseases [1], alone or in combination with other drugs. This thiol drug can also be used to moderate heart failure [2]. It is also sometimes prescribed for angina pectoris (crushing chest pain), Raynaud's phenomenon (a disorder of the blood vessels that causes the fingers to turn white when exposed to cold) and rheumatoid arthritis [3]. Unfortunately, administering captopril for therapeutic purposes leads to undesirable side effects. Preliminary research has indicated significant loss of zinc in urine due to the intake of captopril [4]. Therefore, the determination of this compound is very important.

Several methods have been proposed for the determination of captopril including high-performance liquid chromatography with pre- or post-column derivatization [6–11], colorimetry [5, 12], fluorimetry [13–15], chemiluminescence [16–18], capillary electrophoresis [19–22], and spectrophotometry [23–27]. Electrochemical methods, including amperometry [28] using carbon paste electrode (limit of detection >0.015 μM), differential pulse voltammetry using modified carbon paste electrode (limit of detection >1.1 μM) [29], cathodic stripping voltammetry using Hg electrode (limit of detection >0.5 μM) [30, 31], square wave voltammetry using Hg electrode (limit of detection >0.3 μM) [32], and cyclic voltammetry using boron-doped diamond thin film electrode (limit of detection >25 μM) [33] have been used for captopril determination. Mercury electrode is one of the most widely used electrodes for the voltammetric determination of captopril [30–33]. However, this electrode is poisonous and environmentally is not safe to use.

In this study, we describe the use of ferrocenedicarboxylic acid as a suitable mediator for the electrooxidation of captopril in aqueous media and then as a sensitive and fast tool for captopril determination in pharmaceuticals and urine samples. Also, the suitability of the ferrocenedicarboxylic acid modified carbon paste electrode (FDCMCPE)

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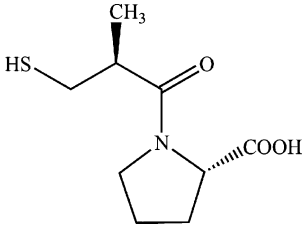
Scheme 1 Structure of captopril



in the electrocatalysis and also determination of captopril are discussed using square wave voltammetry (SWV), cyclic voltammetry (CV), and double potential step chronoamperometry to establish the electrocatalytic behavior of ferrocenedicarboxylic acid. The proposed method is fast, selective, sensitive, and environmentally friendly for determination of captopril in real samples. This amount of detection limit, linear dynamic range, and sensitivity for captopril with the proposed sensor are comparable with the reported electrochemical methods.

Experimental

Reagents and solutions

All the chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout.

A 1.0×10^{-3} M captopril solution was prepared daily by dissolving 0.0224 *g* captopril (97%) in water and dilution the solution to 100 ml with water in a 100-ml volumetric flask. The solution was kept in a refrigerator at 4 °C and in dark. More dilute solutions were prepared by serial dilution with water.

Universal buffer solutions (boric acid, phosphoric acid, acetic acid, and sodium hydroxide, 0.1 M) with different pH values were used for the study of the influence of pH.

High viscose paraffin (density=0.88 g cm^{-3}) from Fluka (Switzerland) was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter= 0.1 mm) from Merck was used as the working electrode substrate. Ferrocenedicarboxylic acid was used from Fluka (Switzerland).

Captopril tablets (Darou Pakhsh Company, Iran, labeled 50 mg captopril per tablet) was purchased from Red Cross drug store in Isfahan.

Apparatus

All the voltammetric measurements were performed using an Autolab PGSTAT 12, potentiostat/galvanostat (Utrecht, The Netherlands) connected to a three-electrode cell, Metrohm (Herisau, Switzerland) Model 663 VA stand, linked with a computer (Pentium IV, 1,200 MHz) and with Autolab software. A platinum wire was used as the auxiliary electrode. FDCMCPE and Ag/AgCl (KCl_{sat}) were used as the working and reference electrodes, respectively.

For the impedance measurements, a frequency range of 100 kHz to 0.10 Hz was employed using the above electrochemical instrument.

pH values were measured with a Metrohm (Model 827 pH-lab) pH meter, equipped with a combined glass electrode (Corning, Model 6.0228.010).

Preparation of real samples

For preparation of tablet solution, ten tablets of captopril labeled with amount of 50 mg per tablet were completely ground and homogenized. Ten milligrams of the powders was accurately weighted and dissolved in 100 ml of water with sonication. After mixing completely, the mixture was filtered with an ordinary filter paper. Then, 10 ml of the filtered solution was transferred into a 100-ml volumetric flask and the solution was diluted to the mark with water. Then, 1.0 ml of the solution plus 4.5 ml of the buffer (*pH* 7.0) were used for the analysis with standard addition method.

The urine samples were analyzed after 1 h of their sampling, except stated. The urine samples were taken from humans and were used for measurements after its centrifuged (3,000 rpm, 25 °C) and diluted two times with water without any further pretreatment. The standard addition method was used for the determination of the captopril contents after dilution of the sample.

Preparation of the sensor

A 2.0% (*m*/*m*) ferrocenedicarboxylic acid spiked carbon powder was made by dissolving the given quantity of ferrocenedicarboxylic acid in diethyl ether and hand mixing with 98 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring. A mixture of 2.0% ferrocenedicarboxylic acid spiked carbon powder plus paraffin oil was blended by hand mixing. The resulting paste was inserted in the bottom of a glass tube (with internal radius 3.0 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without ferrocenedicarboxylic acid was prepared as the above procedure and was used as a blank to determine the background current.

Results and discussion

Electrochemical oxidation of captopril

Captopril, 1-[(2S)-3-mercapto-2-methylpropionyl]-L-proline, is a synthetic dipeptide and is a thiol compound.

Captopril has —COOH and —SH functional groups and the structure is the same as ferrocenedicarboxylic acid. On the other hand, ferrocenedicarboxylic acid is known as a good Ox/Red mediator [34]. Therefore, we thought that ferrocenedicarboxylic acid has the ability to catalyze the oxidation of captopril. We have constructed FDCMCPE by incorporating ferrocenedicarboxylic acid into the carbon paste matrix and its electrochemical properties in a buffered aqueous solution were studied using cyclic voltammetry. The cyclic voltammogram of FDCMCPE exhibits an anodic (E_{pa}=0.48 V) and corresponding cathodic peaks (E_{pc}=0.38 V) related to Fc/Fc^{+} redox couple with quasi-reversible behavior [35]. In addition, the utility of the proposed sensor for oxidation of captopril was evaluated by cyclic voltammetry. The cyclic voltammetric responses of FDCMCPE electrode in 0.1 M universal buffer (pH 7.0), with and without captopril, are shown in Fig. 1 (curves a and b, respectively), whereas the cyclic voltammograms for a bare carbon paste electrode in 0.1 M universal buffer (pH 7.0), with and without captopril, are shown in Fig. 1 (curves d and c, respectively). The results show that the FDCMCPE sensor produces a large anodic peak current in the presence of captopril without a cathodic counterpart. The current observed is associated with captopril oxidation and not the oxidation of surface-attached ferrocenedicarboxylic acid, which is demonstrated by comparing the current in Fig. 1b (without captopril) with those in the presence of captopril in Fig. 1a. It is apparent that the anodic current associated with the surface-attached materials is significantly less than that obtained in the solution containing captopril. In addition, at the surface of a bare electrode, captopril could not oxidize until the potential reached +1.20 V. As can be seen, the electroactivity of captopril on the modified electrode increased significantly with strongly defined peak potential around 490 mV vs. Ag/AgCl electrode. Thus, a decrease in overpotential and enhancement of the peak current for captopril oxidation are achieved with the modified electrodes.

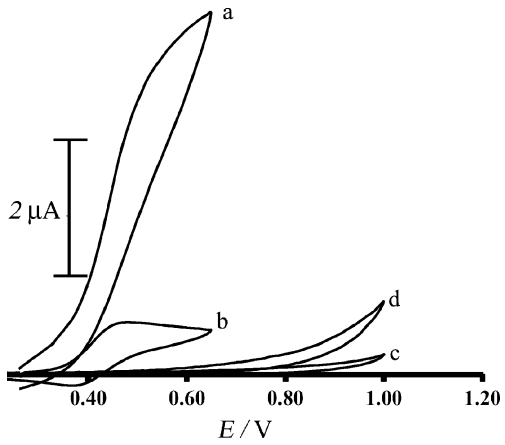


Fig. 1 Cyclic voltammogram of FDCMCPE with scan rate of 10 mV s^{-1} in the buffer solution (pH 7.0). **a** In the presence of 400 μM captopril and **b** in the absence of captopril. (**c**) as (**a**) and (**d**) as (**b**) for an unmodified carbon paste electrode, respectively

Double step potential chronoamperometry was employed for investigating the electrochemical processes of FDCMCPE (Fig. 2a). The current–time curve of the FDCMCPE was obtained by setting the working electrode potential at 0.50 V (at the first potential step) and 0.25 V (at the second potential step) vs. $Ag|AgCl|KCl_{sat}$ in a buffered solution (pH 7.0). The results show very symmetrical chronoamperograms with an equal charge consumed for the oxidation and reduction of the redox couple. The plot of the net electrolysis current vs. $t^{-1/2}$ (Fig. 2b) also showed a straight line which extrapolates close to the origin. Therefore, this type of near-Cottrellian behavior is not due to a linear semi-infinite diffusion process but may be caused by finite diffusion in a thin film, where the near-Cottrell equation behavior can be approximated over a short

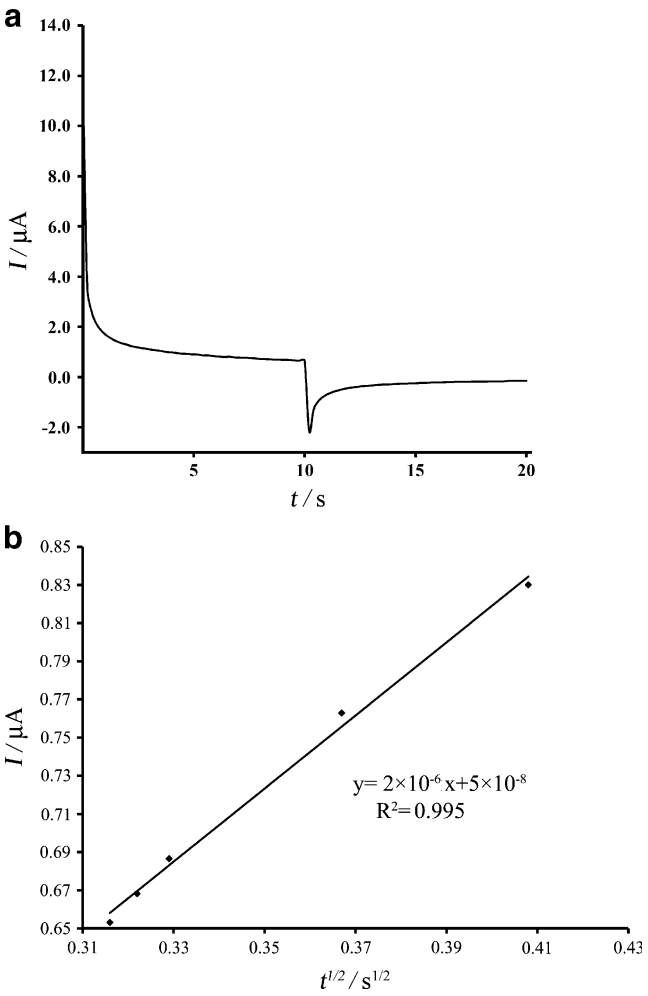


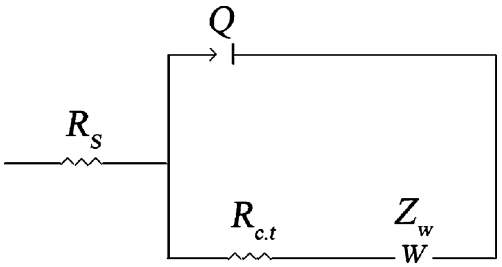
Fig. 2 **a** Double step potential chronoamperogram obtained at the FDCMCPE in the absence of captopril (pH 7.0). First and second potential steps were 0.70 and 0.25 V vs. Ag/AgCl. **b** Cottrell plot for curve (**a**)

time period. Consequently, we can assume diffusion controlled behavior for charge transfer at FDCMCPE, and therefore we use the potential step chronoamperometric experiments to estimate the diffusion coefficient of ferrocenedicarboxylic acid into the paraffin oil. Using Cottrell equation [32], the slope of the linear region of the $I-t^{-1/2}$ plot (in the short time region) produces the apparent diffusion coefficient (D_{app}) of the spiked ferrocenedicarboxylic acid into FDCMCPE:

$$I=nFA_gD_{app}^{1/2}C\pi^{-1/2}t^{-1/2} \quad (1)$$

Where C is the known concentration, D_{app} is the apparent diffusion coefficient of the spiked ferrocenedicarboxylic acid in carbon powder plus paraffin oil, and A_g is the geometric area of this electrode (the diameter, d) of the FDCMCPE (it was calculated according to $(\pi(d/2)^2)$. The apparent diffusion coefficient for ferrocenedicarboxylic acid in carbon paste matrix was found $D=1.81\times10^{-10}$ cm^2 s^{-1} (with $n=1$, $F=96{,}485$ C mol^{-1}, and $A_g=0.091$ cm^2).

Electrochemical impedance spectroscopy is a powerful and very informative technique for probing charge transfer properties at the electrode–solution interface [35, 36]. We have used electrochemical impedance spectroscopy to study FDCMCPE to evaluate its diffusion and/or charge transfer control. Figure 3 indicates the Nyquist plot of the FDCMCPE recorded in the universal buffer (pH 7.0) at the near oxidation peak potential of 0.40 V. The electrical equivalent circuit compatible with the impedance spectra is shown in Scheme 2, which incorporates $R_s=343$ Ω (the solution/electrolyte resistance), $R_{ct}=1{,}014$ Ω (charge transfer resistance), $Z_w=0.1136\times10^{-3}$ (Warburg impedance) related to the semi-infinite linear diffusion, and Q ($Y_0=0.418\times10^{-5}$, $n=0.7273$) (constant phase element). As shown in Fig. 3, the first part showed small charge transfer limitation, whereas the second part (linear part) emphasizes its diffusion control of FDCMCPE. The results showed that the electrode system has both diffusion and charge transfer limitations.



Scheme 2 Equivalent circuit for the system

The catalytic oxidation peak potential gradually shifts towards more positive potentials with increasing the scan rate, suggesting a kinetic limitation in the reaction between the redox site of the ferrocenedicarboxylic acid and captopril. However, the oxidation currents change linearly with the square root of the scan rate, suggesting that, at sufficient overpotential, the reaction is mass transfer controlled. The results show that the overall electrochemical oxidation of captopril at the modified electrode might be controlled by the cross-exchange process between captopril and the redox site of the ferrocenedicarboxylic acid and diffusion of captopril.

pH effect

The electrochemical behavior of captopril in 0.1 M universal buffered solution with different pH values (2.0<pH< 9.0) was studied with FDCMCPE using cyclic voltammetry. Figure 4 shows the variation of I_{pa} vs. pH of the solution. As can be seen, maximum electrocatalytic current was obtained at pH 7.0. The electrocatalytic effect of ferrocene derivatives decreased in higher pH values [35]. Therefore, pH 7.0 was selected as the optimum pH for the

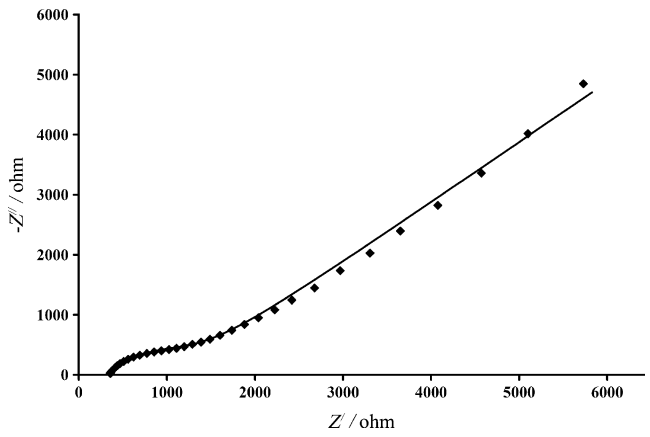


Fig. 3 Impedance plot for the FDCMCPE system in a pure buffer (pH=7.0) solution with E_p of +0.40 V vs. Ag/AgCl reference electrode. Bias is 0.40 V with $E_{ac}=5$ mV with frequency range of 10 kHz to 1 Hz

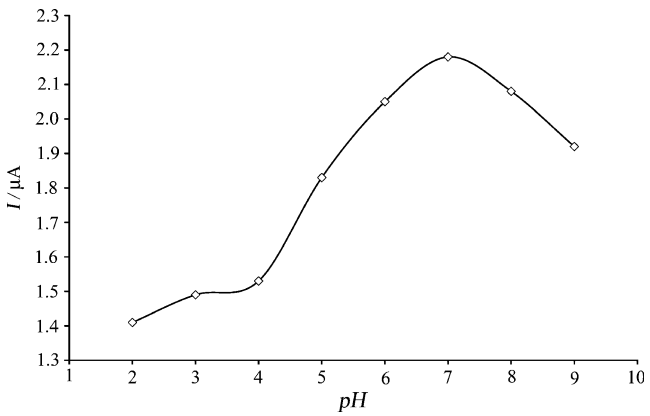


Fig. 4 Current vs. pH curves for electrooxidation of 15.0 μM captopril with different pH at the surface of FDCMCPE with a scan rate 10 mV s^{-1}

electrocatalysis of captopril oxidation at the surface of FDCMCPE.

Prior to using FDCMCPE for the electrocatalytic oxidation of captopril in real samples, the rate of loss of electrochemical activity for this electrode was investigated. This rate was evaluated by noting any decrease in the anodic charge, q_a, in consecutive potential scan cycles. The results showed that the anodic and cathodic peak currents of ferrocenedicarboxylic acid/ferriceniumdicarboxylic acid couple decreased; consequently, the electrochemical activity of FDCMCPE was reduced during successive scans, without any change in the half-wave potential, $E_{1/2}$. The decrease in electrochemical activity may be due to the removal of ferriceniumdicarboxylic acid ion generated at the electrode by dissolution into the aqueous solution. Therefore, surface regeneration of FDCMCPE before each experiment is necessary.

Electrocatalytic determination of captopril

Since square wave voltammetry (SWV) has a much higher current sensitivity than cyclic voltammetry, SWV (with increment potential of 6 mV, amplitude potential of 10 mV, and frequency of 20 Hz) was used to estimate the lower range of detection and the linear calibration range of captopril. The results showed two linear segments with different slopes for captopril concentrations. For the concentration range of 0.30–1.95 μM captopril, the regression equation was $I(\mu A) = 355.770C_{\text{Captopril}} + 0.0478(r = 0.9864, (n = 10))$ and for the captopril concentration range of 2.62–140.0 μM, the regression equation was $I(\mu A) = 10.701C_{\text{Captopril}}0.755(r = 0.9927, (n = 11))$, where $C_{\text{Captopril}}$ is mM of captopril.

Finally, the detection limit (according to the definition of $Y_{LOD} = Y_B + 3s$, the average blank signal plus three times of its standard deviation (n=10)) [37] was obtained 9.1×10^{-8} M captopril by SWV methods.

The surface of FDCMCPE should be regenerate before each experiment. Therefore, the reproducibility of the sensor was evaluated using the replicate signals (n=10) of the electrode for 5.0 μM captopril. The relative standard deviation for ten replicate measurements of 5.0 μM captopril was 1.0%.

Interference studies

Interference studies were carried out with several chemical substances prior to the application of the proposed method for the assay of captopril in urine samples and tablet. The potential interfering substances were chosen from the group of substances commonly found with captopril in pharmaceuticals and in biological fluids. The influence of various substances as potential interference compounds on the determination of 50.0 μM captopril under the optimum conditions was studied. Tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than 5% for determination of captopril. The results are given in Table 1, which shows the peak current of captopril is not affected by all conventional cations, anions, and organic substances.

Determination of captopril in real samples

In order to evaluate the applicability of the proposed sensor for the determination of captopril in real samples, we have examined the ability of the electrochemical sensor for the determination of captopril in tablet and urine samples using standard addition method. The samples were also analyzed by a standard method including potentiometric titration with potassium iodate [38]. The results for the tablet sample analysis are given in Table 2. In addition, the results obtained for the urine samples by the proposed method were compared with the standard method statistically, using Student's t test (for the accuracy), and variance ratio, F test (for the precision) at 95% confidence level. The results are given in Tables 3. A typical SWV for the determination of captopril in a urine sample (Table 3, row no. 3) is shown in Fig. 5. Those results demonstrated the ability of FDCMCPE for voltammetric determination of captopril in real samples with the good recoveries of the spiked captopril and good reproducibility. The presence of some positive errors on the urine samples after spike of captopril may be due to the presence of some thiol compounds in the urine.

Conclusion

The electrochemical behavior of FDCMCPE as a new electrochemical sensor for captopril determination has been studied using cyclic voltammetry, chronoamperometry, and impedance spectroscopy. It has been found that, with cyclic voltammetry, the oxidation of captopril occurred at a potential about 490 mV on the surface of the modified

Table 1 Interferences study for the determination of 50.0 μM captopril under the optimized conditions

Species	Tolerance limits ($m_{\text{substance}}/m_{\text{captopril}}$)
Glucose, saccharose, lactose, fructose, K^+, Na^+, CO_3^{-2}, Ca^{2+}, Mg^{2+},ClO_4^-, SO_4^{2-}, F^-, Cl^-	1,000[a]
Urea	400
Fe^{+2}, Fe^{+3}, L-threonine, L-phenylalanine, glycine, methionine, alanine	200
L-Tryptophane	50

[a] Maximum concentration of species tested

Table 2 Determination of captopril in tablet sample (n=3)

Sample	Added (μM)	Expected (μM)	Found (μM)	Standard method (μM)
Tablet[a]	–	10.0	9.65±0.34	9.85±0.54
	20.0	30.0	30.65±0.56	–
	40.0	50.0	50.62±0.42	–
	50.0	60.0	60.93±0.87	–

[a] 50 mg tablet, Darou Pakhsh Company, Iran

Table 3 Concentration values obtained from the proposed and the reference method for captopril analysis of urine sample using the proposed method under optimum conditions (n=3)

Sample	Proposed method (μM)	Standard method (μM)	F_{ex}	$F_{tab(0.05),(2,2)}$	t_{ex}	$t_{tab(98\%)}$
Urine[a]	8.1±0.8	8.0±0.5	3.1	19	3.3	3.8
Urine[a]	8.3±0.9	8.2±1.1	3.5	19	3.4	3.8
Urine[b]	2.3±0.5	2.2±0.6	2.6	19	3.1	3.8
Urine[b]	2.1±0.4	2.1±0.4	2.1	19	2.9	3.8
Urine[c]	4.2±0.5	4.1±0.7	2.1	19	2.8	3.8
Urine[c]	4.1±0.4	4.0±0.8	1.9	19	2.3	3.8

± Shows the standard deviation
[a] Sampling was made after 2.5 h from a man who is safe and used captopril
[b] Sampling was made after 2.5 h from a man who had heart problem and used captopril
[c] Sampling was made after 2.5 h from a man who had kidney problem and used captopril

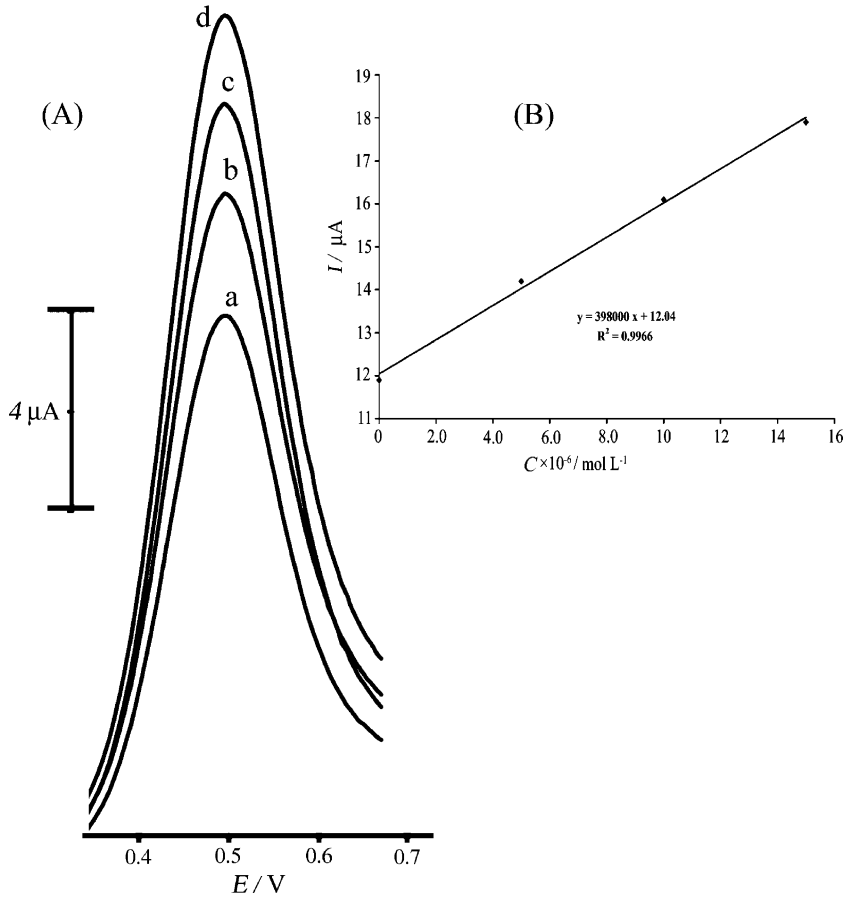


Fig. 5 Square wave voltammograms of FDCMCPE in a solution containing 9.0 ml of the buffer (pH 7.0) and 1.0 ml of a urine sample for row no. 3 from Table 3. Captopril added as **a** 0.0, **b** 5.0, **c** 10.0, and **d** 15.0 μM

carbon paste electrode, while the oxidation captopril does not takes place at the surface of a bare carbon paste electrode up to +1.20 V. The proposed method is sensitive to detect captopril as low as 0.091 μM. The proposed method was also used as a selective, simple, and precise new sensor for voltammetric determination of captopril in real samples such as drug and urine.

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